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(Quarterly Report)

EMBRITTLEMENT OF METALS
BY ORGANIC LIQUIDS

Commanding Officer
Frankford Arsenal
Philadelphia 37, Pennsylvania

Contract No. DA-11-ORD-022-3108

IIT RESEARCH INSTITUTE
Technology Center
Chicago 16, Illinois

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June 1, 1963 - August 31, 1963

for
Commanding Officer
Frankford Arsenal
Philadelphia 37, Pennsylvania

Attention: Mr. J M. McCaughey
Pitman-Dunn Laboratories

September 16, 1963

EMBRITTLEMENT OF METALS BY ORGANIC LIQUIDS

ABSTRACT

It is shown that embrittlement of high strength steel can be revealed by the use of a deeply and sharply notched specimen in tension-tension fatigue. Test results show a relationship between degree of embrittlement and the length of long chain alcohols. In this series water appears to behave as an alcohol. Moreover, the embrittlement by water is essentially independent of pH and the presence of saline solutes.

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EMBRITTLEMENT OF METALS BY ORGANIC LIQUIDS

I. INTRODUCTION

This is the third quarterly report summarizing progress in one portion of a composite program entitled "Fracture of Metals," identified under Contract No. DA-11-ORD-022-3108. This report covers the period June 1, 1963, to August 31, 1963.

This portion of the program on "Fracture of Metals" is directed to explore the existence and nature of embrittlement which might be produced by concurrent exposure of metals to organic liquids and tensile stresses. Organic liquids are defined for present purposes as pure liquid species, miscible liquids, and solutions of solids in liquids. Embrittlement constitutes the premature incidence of cracking as experienced under continuously increasing load, static loading, or dynamic (cyclic) loading. "Premature" implies a lower maximum load, a shorter time, or fewer cycles than would be expected for the material in air.

Thus far, using more than 100 distinct organic species in conjunction where necessary with one or more of 6 solvents and representing about 27 categories of compound, no premature failures were encountered in continuous loading tensile tests and in static, unnotched loading at the yield point. This conclusion applies both to a high-strength, heat-treated, low-alloy carbon steel and to a high-strength, heat-treated aluminum alloy.

Significant embrittlement has been encountered in the fatigue testing of the high-strength steel* in a severely notched condition. Using the endurance limit defined in the previous report for this material, tests are conducted at a single stress regime (12,500 psi preload in tension plus 0 to 4370 psi tension cyclically), which in air will not produce failure in many millions of cycles. The number of cycles to failure is therefore a measure of embrittlement.

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* Commercial designation: 300M. Chemical composition: 0.4% C, 1.6% Si, 0.75% Mn, 0.85% Cr, 1.85% Ni, 0.4% Mo, 0.08% V. Quenched and tempered to 200,000 psi yield strength.

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While the nominal stresses imposed on the edge-notched sheet specimen are not large, the depth of notch and the notch radius (about 0.001 in.) are such as to create very large stress magnifications at the root. If one assumes purely elastic behavior, the stress magnification is probably between 20X and 30X. This means that the stresses at the notch root reach a maximum value of about 400,000 psi.

Testing in air under these conditions, 7,500,000 cycles have been run without evidence of cracking. Two organic liquids, heavy mineral oil and dioxane, appear also to have no propensity for inducing premature cracking. These two liquid species are thus useful as inert solvents for more active organic species. The test results are thus useful as inert solvents for more active organic species. The test results are presented here in groupings which permit interpretation rather than in the chronological order of their occurrence.

II. INFLUENCE OF WATER ON FATIGUE LIFE OF HIGH-STRENGTH STEEL

Distilled water induces fatigue failure under the specific conditions of test at 583,000 cycles. This is a profound embrittlement but one which is no novelty to the subject of high-strength steels. The origin of water embrittlement is generally regarded as falling within the context of what is termed "stress-corrosion" cracking. Contemporary theory of stress-corrosion cracking treats the mechanism as one of the highly localized electrochemical corrosion accelerated and guided by the intensity and direction of principal tensile stresses.

However, the substance of the present results sheds considerable doubt on the applicability of stress-corrosion theory to water embrittlement. The addition of 5% NaCl to water as a solution produces fatigue failure in 530,000 cycles, which is not distinguishably different from distilled water. Yet clearly the electrical conductivity of the saline solution is orders of magnitude greater than that of distilled water.

Further tests reveal no significant influence of pH of water on fatigue limit. Distilled water exposed to air assumes a pH of about 4 probably because of CO_2 absorption in minute amounts. The pH of distilled water was adjusted to one by the addition of a few drops of HCl in one instance and to 7 and 12 by the addition of drops of concentrated NaOH solution. The results of fatigue testing using these four pH levels are shown in Figure 1, where it may be seen that over the range of pH from 1 to 12 the influence of hydrogen and hydroxyl ion concentration is very small and probably negligible when the normal scatter of fatigue data is taken into account. Added to the negligible influence of a high salt concentration, one can draw the conclusion that ion concentration is not a significant factor. This conclusion is, of course, quite incompatible with contemporary stress-corrosion theory.

III. INFLUENCE OF PRIMARY, SECONDARY, AND TERTIARY ALCOHOLS ON THE FATIGUE LIFE OF HIGH-STRENGTH STEEL

The following alcohols as pure, dry liquid species have been used to study their influence on fatigue life:

Primary Alcohols	Cycles to Failure
methanol	796,000
ethanol	935,000
n-butyl	1,126,000
n-amyl	1,075,000
isoamyl	1,172,000
n-octyl	4,533,000

The primary alcohols consistently produce fatigue embrittlement, and there is an apparent progression toward less effect with increasing molecular weight. This progression could be amplified by the addition of test results with n-propyl, n-hexyl and n-heptyl alcohols, and this will be done very shortly.

A second progression is observed with certain secondary alcohols:

Secondary Alcohol	Cycles to Failure
sec-propyl	769,000
sec-amyl	892,000
sec-octyl	1,193,000

The saturated alcohols can be described by the general formula $C_nH_{2n+1}OH$, so that when n = 1 we have CH_3OH (which is methanol) and when n = 8 we have $C_8H_{17}OH$ (which is octyl alcohol). However, the formula

$C_8H_{17}OH$ satisfies a whole group of alcohols of similar molecular weight but different physical properties. The different physical properties derive from variations in symmetry of carbon and hydroxyl bonding.

The primary, secondary, and tertiary alcohols have a common property defined in terms of the coordination of carbon atoms about that carbon atom to which the OH group is attached. The carbon atom associated with the OH group in primary alcohols has a carbon coordination of one; in secondary alcohols, a carbon coordination of two; and in tertiary alcohols, a carbon coordination of three. Thus one of the primary amyl alcohols could be described as follows:

```
      H   H   H   H   H
      |   |   |   |   |
  H - C - C - C - C - C - OH
      |   |   |   |   |
      H   H   H   H   H
```

but a simple variation such as (the hydrogen atoms are omitted)

```
C - C - C - C - OH
    |
    C
```

does not change the carbon coordination at the OH group and so constitutes another primary amyl alcohol with different physical properties. The first of these is commonly called n-amyl alcohol and for obvious reasons is described as a straight-chain alcohol. The second is called isoamyl alcohol.

The straight-chain secondary alcohol, sec-amyl, has the following arrangement (again omitting hydrogen atoms) between carbon atoms and the OH group:

```
C - C - C - C - C
            |
            OH
```

The carbon coordination of the carbon atom holding the OH group is two. When this becomes three, as follows:

```
        C
        |
C - C - C - C
        |
        OH
```

We have tert-amyl alcohol which is, strictly speaking, no longer a straight-chain molecule

Obviously the multiplicity of alcohol species goes up with molecular weight, and a study of embrittlement might get mired in irrelevancies if every species were taken for study. For the purposes of this program, simplified trends are the objective.

A clear and simple trend is revealed by plotting the cycles to failure against the numerical value of n from the formula $C_nH_{2n+1}OH$ as in Figure 2. Two curves are plotted - one for the primary and one for the secondary alcohols. Whether the trend for primary alcohols is discontinuous at n-octyl or curves upward steeply requires more data. The cycles to failure N_F for n-amyl seems low compared to the curve, but it may be that commercial purity n-amyl alcohol contains some sec-amyl alcohol. This point must be checked.

It is most remarkable that when the curves for both primary and secondary alcohols are extrapolated back to n = 0, the value of N_F coincides almost exactly with that for distilled water. For the purposes of embrittlement, this suggests that water behaves as a limiting species of alcohol. This is another strong indication that stress-corrosion concepts are incorrect.

While the correlation of fatigue life with the number of carbon atoms in the alcohol molecule is a valuable sign of systematic behavior, it does not of itself shed much light on the mechanism of embrittlement. The common denominator in all of these alcohols is the existence of an OH group. But the oxygen atom is about four times as big as the hydrogen atom so that the OH group is really dominated by the size of the oxygen atom and might be regarded effectively as such. Whether other groups associated with oxygen have a similar effect remains to be seen. Since metals have a strong affinity for oxygen, it's reasonable to suggest that active influence of alcohols on the cohesive strength of iron derives from interaction between surface atoms of iron and the OH groups of the alcohol. The influence of the OH group can be seen from a comparison of ethanol, whose cycles to fracture (N_F) was 935,000, with ethylene glycol, whose structure is very similar but possesses two OH groups. In this case the number of cycles to failure (N_F) is 824,000. Ethylene glycol behaves somewhat as if it were a double methanol: $(CH_2OH)_2$

Given this premise, a free surface of iron will draw to itself a monolayer of adsorbed molecules oriented such that the OH groups are attached to the iron atoms or at suitable interatomic packing sites.

We must wonder now how molecular size and shape influences the ability to create a high packed density of adsorbed and oriented molecules on the surface of a metal. We must also wonder as to what extent the size and shape of a molecule will influence its ability to follow a crack into the interior of a metal as it propagates.

An approach to this will be made by choice of various alcohol species with peculiar structural characteristics or trends in structure. For example, we can compare primary, secondary, and tertiary amyl alcohols:

Alcohol	Cycles to Failure
n amyl	1,075,000
isoamyl	1,172,000
sec-amyl	892,000
tert amyl	1,530,000

In this set of results and also in Figure 2, it is seen that the secondary alcohols behave as if they were shorter in the carbon chain length; they behave as if the longest chain attached to the hydroxyl carbon were the only factor.

Benzyl alcohol can be regarded as methanol with an attached benzene ring. This has a definite effect in reducing embrittlement; for while methanol causes failure in 796,000 cycles, benzyl alcohol requires 1,133,000 cycles. These experiments are, of course, too few and many more exploratory studies are needed.

IV. INFLUENCE OF ACTIVE SOLUTIONS ON FATIGUE LIFE OF HIGH-STRENGTH STEEL

In going from a pure liquid species to solutions, we open up a variety of interesting alternatives and possibilities such as:

- solution of an active component in an inactive solvent;
- solution of two active components;
- competition in adsorption between embrittling and non-embrittling species

Figure 3 illustrates the behavior of solutions of an active component, isoamyl alcohol, with an inactive component, heavy mineral oil. The trend shows an independence of concentration of the isoamyl alcohol above a critical 10% level. This is the expected behavior of a solution in which one component has a propensity for surface adsorption. The existence of a threshold concentration requires some consideration. It may be as in vapor condensation processes that the desorption rates and absorption rates have different concentration dependencies and that, as a result, the equilibrium concentration of isoamyl molecules on the iron surface is too small at the threshold.

Figure 4 illustrates the behavior of two miscible active liquids -- water and ethanol. The shape of the curve indicates that water adsorbs to an iron surface to a degree in excess of its proportion in the solution. It may be that all solutions of active components will show this characteristic. If this is the case, then it must be inferred that the adsorption bond strength and embrittling propensity are directly proportional.

V. FAILURE UNDER STATIC LOADING AND HEAVY NOTCH SEVERITY

It is appropriate to wonder whether the premature failure of a deeply and sharply notched specimen in cyclic loading is due to the cyclic nature of the loading or the stress levels attained in the notched condition. Certainly, the dynamic character of cyclic fatigue assists in repetitively rupturing intervening oxide films. Some preliminary tests have been made in static loading using the same V-notched specimen. At stresses of about 90% of the ultimate strength, water, methanol, and ethanol produce delayed failure in minutes to hours. Under the same conditions the steel specimen has supported the load for 72 hours without sign of failure. This work is being amplified, but it is already clear that stress magnification by itself can produce embrittlement. The cyclic character of dynamic fatigue is therefore not in itself fundamental to the embrittlement process.

VI. PERSONNEL AND LOGBOOKS

The research program is under the supervision of the writer with technical consultation by Mr. R. Crouse, Senior Chemist, and J. Garner, Associate Chemist. The work itself is being performed by Mr. R. Sarocco, Technician. The results reported are contained in IITRI Logbook No. C 13536.

Respectfully submitted,

IIT RESEARCH INSTITUTE

W. Rostoker

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WR:jw

Tech Rev. JFR

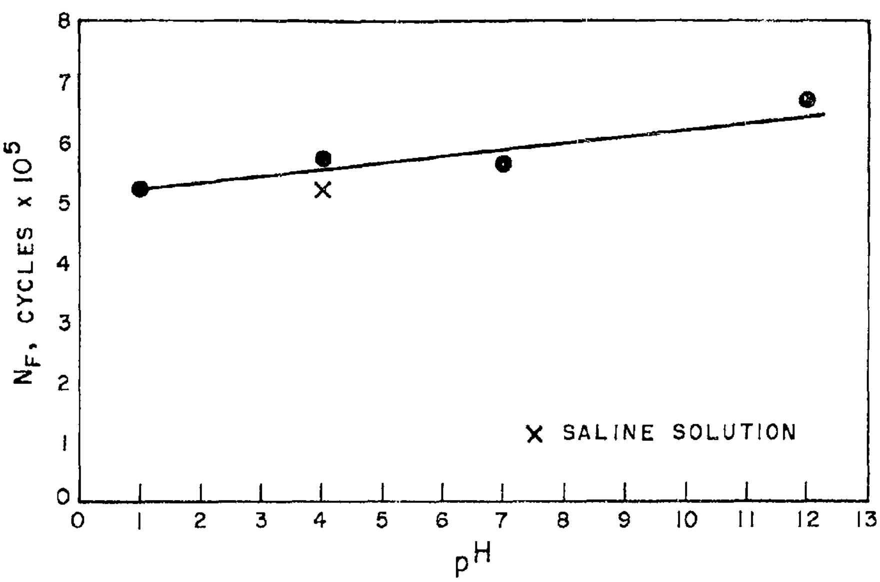

FIG. 1 - INFLUENCE OF THE pH OF WATER ON THE FATIGUE LIMIT OF HIGH-STRENGTH STEEL V-NOTCHED TENSION-TENSION SPECIMEN. 12,500 psi preload, 4370 psi dynamic load.

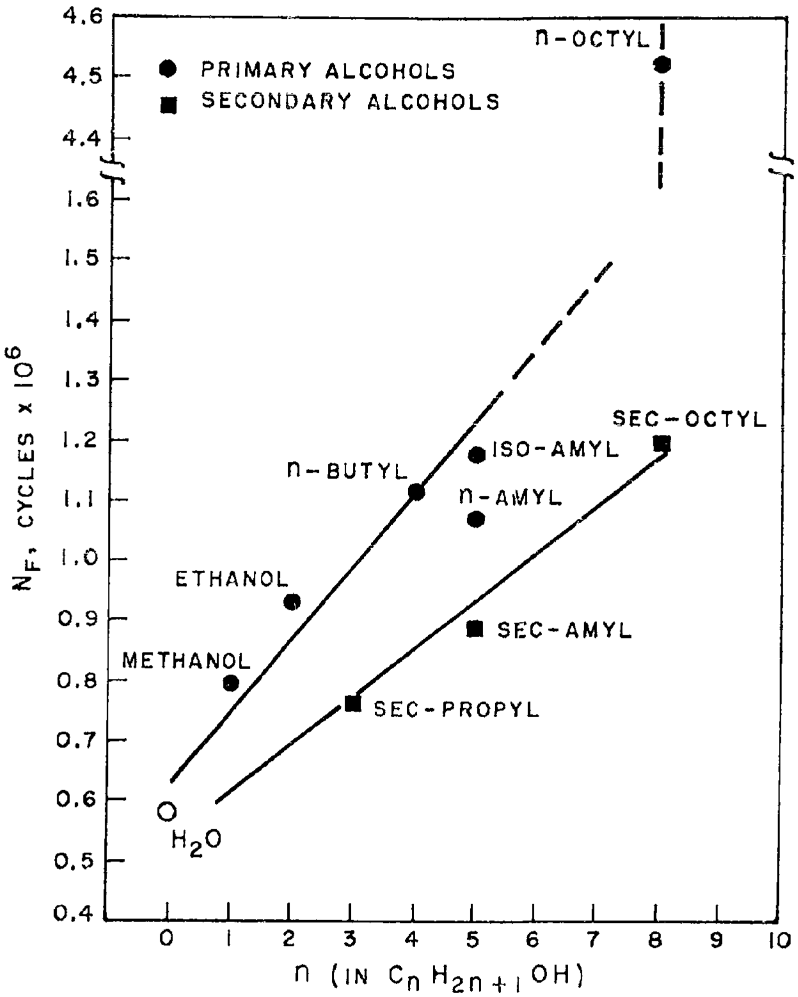

FIG. 2 - FATIGUE LIMIT (N_F) FOR PRIMARY AND SECONDARY ALCOHOLS. High-strength steel. V-notched tension-tension specimen. 12,500 psi preload, 4370 psi dynamic load.

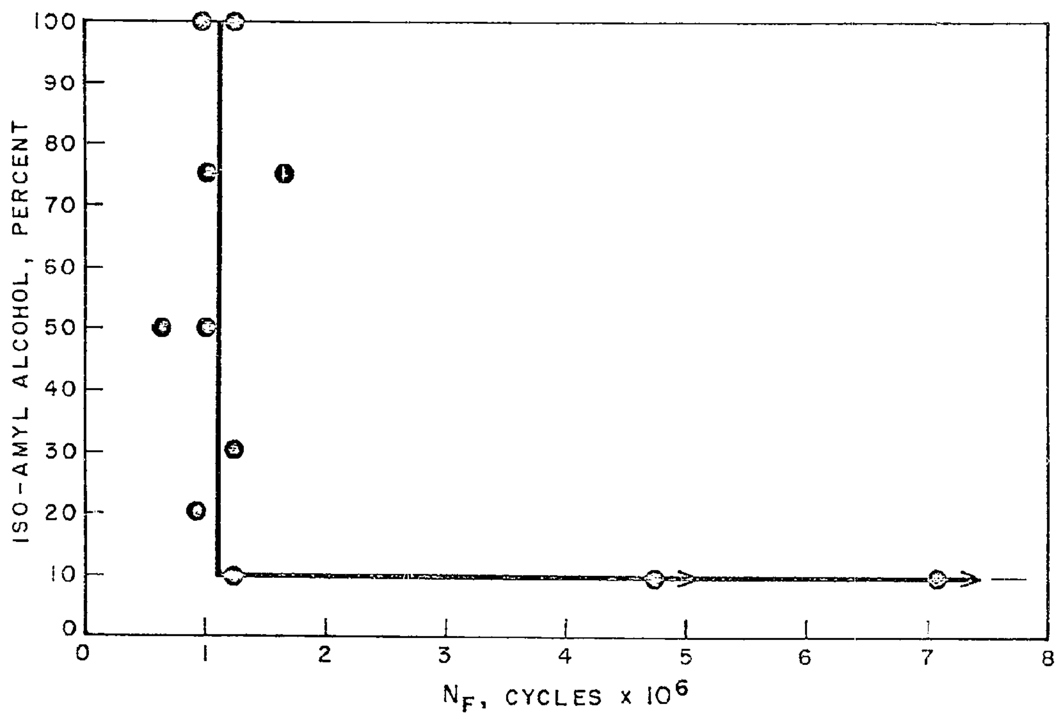

FIG. 3 - NUMBER OF CYCLES TO FAILURE, N_F, AS A FUNCTION OF ISO-AMYL ALCOHOL CONCENTRATION IN HEAVY MINERAL OIL. V-notched tension-tension fatigue specimen. High-Strength steel. 12,500 psi preload plus 4370 psi dynamic load.

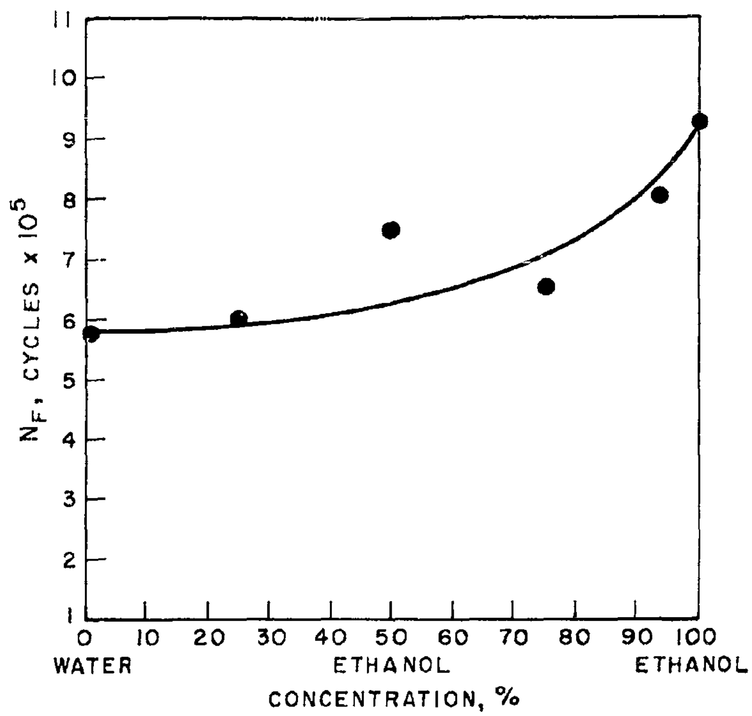

FIG. 4 - NUMBER OF CYCLES TO FAILURE, N_F, IN WATER-ETHANOL SOLUTIONS. V-notched tension-tension fatigue specimen. High-strength steel. 12,500 psi preload, 4370 psi dynamic load.